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厦门大学

硕士学位论文

**地热水条件下砷在纳米级 A 型活性氧化铝  
表面的吸附机理研究**

**Study of Arsenic Adsorption Mechanism on Nanoscale  
A-type Activated Alumina in Geothermal Water**

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## 摘要

砷是一种以高毒性而闻名的类金属元素,水环境中的砷对人体健康和生态环境造成严重危害。近年来随着地热水开发利用的不断扩大,来源于地热水的砷污染引起国内外研究者的更多注意。大规模开发伴随的高砷地热弃水直接排放是砷污染的原因之一,因此在高水温和多组分共存条件下对砷进行选择吸附可以满足地热水条件下除砷的需要。

本研究以纳米级 A 型活性氧化铝(Nanoscale A-type Activated Alumina, NAAA)为吸附剂,研究不同地热水温下 NAAA 吸附砷的动力学以及 pH 和离子强度变化对 NAAA 吸附砷的影响,结合 X 射线衍射(X Ray Diffraction, XRD)和傅立叶变换红外光谱(Fourier Transform Infrared Spectroscopy, FTIR)对吸附砷前后的 NAAA 进行表征,探讨砷吸附反应机理。研究结果表明:

(1) 除个别情况以外,在室温下,所研究的 pH 和离子强度范围内, NAAA 吸附砷的过程趋向于化学吸附。除地热水温为 363 K 时 NAAA 吸附 As(III)的情况以外, NAAA 对砷的吸附动力学曲线都可分为 3 个阶段, NAAA 吸附 As(III)的过程可能为放热过程,吸附 As(V)的过程可能为吸热过程且可能对 As(V)有专属吸附作用。

(2) 除地热水温为 303 K 时 NAAA 吸附 As(III)的情况以外,在所研究地热水温下, NAAA 对 As(III)的吸附动力学数据在初始阶段更符合拟一级动力学模型,对 As(V)的吸附动力学数据在初始阶段更符合 Elovich 方程。除地热水温为 363 K 时 NAAA 吸附 As(III)的情况以外, NAAA 吸附砷的动力学全过程数据均符合拟二级动力学模型。除地热水温为 303 K 时 NAAA 吸附 As(III)的情况以外,颗粒内部扩散过程可能是 NAAA 吸附砷的速度控制过程;当  $\text{pH}=5.0\pm0.1$  时, NAAA 对 As(V)的吸附属于物理吸附。当  $\text{pH}=9.0\pm0.1$  时, NAAA 对 As(III)的初始吸附速率和整体吸附速率均随地热水温升高而增大;当  $\text{pH}=5.0\pm0.1$  时, NAAA 对 As(V)的初始吸附速率随地热水温升高而增大,但整体吸附速率随地热水温升高基本不变。

(3) XRD 分析表明所使用的 NAAA 符合标准谱图, 2 个最强衍射峰分别对应于(202)和(300)晶面, 实验样品谱图的衍射峰明显宽化表明其结晶度差, 为非晶态结构, 且晶粒尺寸小。在 NAAA 吸附 As(III)过程中是高地热水温(363 K)而不是 As(III)使 NAAA 晶体结构发生了变化。随着地热水温升高, NAAA 吸附 As(V)后没有发生晶体结构上的变化。FTIR 分析表明 NAAA 吸附 As(V)的过程属于外层吸附, 吸附 As(III)的过程属于内层吸附。砷容易与 NAAA 的 B 型羟基发生反应。由于表面效应和表面悬键增加, 常规氧化铝指纹区的谱峰在结晶度差的 NAAA 中完全消失且出现明显的蓝移和宽化。NAAA 对砷的吸附机理趋向于以化学吸附为主的特性吸附, 且升高温度有利于吸附反应。

关键词: 纳米级 A 型活性氧化铝; 砷; 地热水; 吸附机理

## Abstract

Arsenic is a metalloid element that is famous for its high toxicity; the arsenic that exists in water environment has great harm to human body and ecological environment. In recent years, with the expansion of the development and the utilization of the geothermal water, the arsenic pollution that comes from the geothermal water has drawn more attention from the researchers at home and abroad. The large-scale development that combined with the direct discharge of the geothermal wastewater that its arsenic content is high becomes one of the reasons for the arsenic pollution. So in the condition of the high water temperature and the multi-composition coexistence, the selective adsorption of arsenic could meet the need of the arsenic removal of the geothermal water.

The research uses the Nanoscale A-type Activated Alumina(NAAA) as the adsorbent, explores the kinetics of the arsenic adsorption on the NAAA and the effects of the change of the pH and the ionic strength for the arsenic adsorption on the NAAA at different temperatures of the geothermal water, combined with the X Ray Diffraction(XRD) and the Fourier Transform Infrared Spectroscopy(FTIR) to characterize the NAAA that without and with arsenic adsorpted, discusses the reaction mechanism of the arsenic adsorption. The results of the research show that:

(1) Except for individual circumstances, at the room temperature, in the range of the pH and the ionic strength studied, the processes of the arsenic adsorption on the NAAA tend to be the chemical adsorption. Except for the As(III) adsorption on the NAAA while the temperature of the geothermal water is 363 K, the adsorption kinetic curves of the arsenic adsorption on the NAAA all can be divided into three stages, the processes of the As(III) adsorption on the NAAA may be the exothermic processes, the processes of the As(V) adsorption on the NAAA may be the endothermic processes and the As(V) adsorption on the NAAA may be the exclusive adsorption.

(2) Except for the As(III) adsorption on the NAAA while the temperature of the geothermal water is 303 K, at the temperatures of the geothermal water studied, the kinetic data of the As(III) adsorption on the NAAA is more in line with the pseudo-first order kinetic model in the initial stage, the kinetic data of the As(V) adsorption on the NAAA is more in line with the Elovich equation in the initial stage. Except for the As(III) adsorption on the NAAA while the temperature of the geothermal water is 363 K, the data of the arsenic adsorption on the NAAA is all compliance with the pseudo-second order kinetic model in the whole process. Except for the As(III) adsorption on the NAAA while the temperature of the geothermal water is 303 K, the processes of the intra-particle diffusion may be the speed control processes of the arsenic adsorption on the NAAA. When the  $\text{pH}=5.0\pm0.1$ , the As(V) adsorptions on the NAAA belong to the physical adsorption. When the  $\text{pH}=9.0\pm0.1$ , the initial rate and the whole rate of the As(III) adsorption on the NAAA both increase as the temperature of the geothermal water rises; when the  $\text{pH}=5.0\pm0.1$ , the initial rate of the As(V) adsorption on the NAAA increases as the temperature of the geothermal water rises, but the whole rate of the As(V) adsorption on the NAAA basically doesn't change as the temperature of the geothermal water rises.

(3) The XRD analysis indicates that the NAAA used is in line with the standard spectrum, two of the strongest diffraction peaks corresponds to the (202) and the (300) crystal face, the significant broadening of the diffraction peaks of the spectra of the experimental samples indicates that the crystallinity of the samples is poor, the crystal structure of the samples is amorphous state and the grain size is small. In the processes of the As(III) adsorption on the NAAA, it's the high temperature of the geothermal water (363 K) not the As(III) makes the crystal structure of the NAAA change. As the temperature of the geothermal water rises, after the As(V) adsorption, the crystal structures of the NAAA don't change. The FTIR analysis indicates that the processes of the As(V) adsorption on the NAAA belong to the outer-sphere adsorption, the processes of the As(III) adsorption on the NAAA belong to the inner-sphere adsorption. Arsenic is easy to react with the B-type hydroxyl of the NAAA. As a

result of the surfacial effect and the increase of the surfacial dangling bond, the peaks that in the fingerprint region of the conventional alumina completely disappear in the NAAA that its crystallinity is poor, and the obvious blue shift and the obvious broadening emerges. The mechanism for the arsenic adsorption on the NAAA tends to be the exclusive adsorption that the chemical adsorption predominates, and the rise of the temperature is conducive to the adsorption reaction.

**Key Words:** Nanoscale A-type Activated Alumina; Arsenic; Geothermal Water; Adsorption Mechanism

## 第 1 章 绪论

### 1.1 引言

地热水作为一种新型能源和宝贵的水资源,与其它常规能源相比较,具有分布广、成本低、易于开采,并可直接利用等优点<sup>[1]</sup>。2007 年,全国地热(浅层地热能)开发利用现场经验交流会明确指出全国每年可开发利用的地下热水资源总量约 68.45 亿立方米,所含热能量为  $9.72 \times 10^{17}$  焦,折合每年 3284.8 万吨标准煤的发热量<sup>[2]</sup>。地热水中的砷由于其高毒性和致癌性,对人体危害极大,被国内外研究者所广泛关注。因此,研究地热水条件下砷的去除对提高地热水的利用价值、保护人类健康和环境具有重要意义。本课题对中高温地热水条件下纳米级 A 型活性氧化铝(Nanoscale A-type Activated Alumina, NAAA)对砷的吸附情况进行研究,发掘其作为地热水除砷材料的应用潜力。

### 1.2 砷概述

#### 1.2.1 砷的基本性质

砷(As)是一种灰色类金属元素(metalloid element),原子序数为 33,元素周期表中第四周期第五主族元素,位于磷锑之间,理化性质似磷,能形成合金,又易于碳、氢、氧共价化合,特性介于典型金属和非金属之间。它的相对原子质量是 74.9216,相对密度是  $5.727 \text{ g/cm}^3$ (20 °C),熔点 817 °C,沸点 616 °C,砷有黄、灰、黑三种同素异形体,在室温下最稳定的是灰色的、菱形的金属型的  $\alpha$ -砷,化学活性不高,不溶于水,有较好的传热和导电性能,常温时在空气中缓慢的氧化,呈粉末状的砷与氧化剂混合时能迅速的燃烧生成三氧化二砷<sup>[3]</sup>。基态砷原子的电子层结构为  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$ ,测得基态谱项为  $^4S$ ,表明它有三个单电子占据的轨道,即价电子层结构为  $4s^2 4p_x^1 4p_y^1 4p_z^1$ <sup>[4]</sup>,可以表现出多种价态,最常见的是-3、0、+3 和+5 价,主要价态为+3 价和+5 价。

自然界中砷极少以单质状态存在，砷在地壳中的含量约为 1.5-3 mg/kg，排第 20 位，海水中排第 14 位，人体中排第 12 位<sup>[5]</sup>。除发现少量的天然砷外，已知有 300 多种含砷矿物，最普通的矿物是砷化物矿、硫化物矿、砷酸盐矿。此外，海水中平均含有 1.1 μg/L 的砷，在矿泉水、土壤和人体中都有微量的砷<sup>[6]</sup>。

### 1.2.2 水体中砷的存在形态

环境中的砷以无机和有机状态存在，一般认为有机砷是无毒的，而无机砷具有毒性作用。在自然水体中，砷主要以无机砷形式存在，而砷的有机化合物含量一般都比较低，除非人类活动造成了较严重的有机砷污染<sup>[7]</sup>。无机砷主要以亚砷酸盐(Arsenite, As(III))和砷酸盐(Arsenate, As(V))形态存在，As(III)比 As(V)的毒性高 60 倍<sup>[8]</sup>。存在于地表水和地下水中的 As(III)和 As(V)在较宽的 pH 范围内都处于可溶性状态。在有氧条件下，As(V)更为稳定，是砷的主要存在形式；而在无氧条件下，As(III)是主要存在形式。氧化还原电位(Eh)和酸碱度(pH)是控制水溶液中砷的形态分布的主要因素。

图 1.1 为水温为 298 K 时 As-O<sub>2</sub>-H<sub>2</sub>O 系统中砷的形态分布，横坐标为酸碱度(pH)，单位为无量纲；纵坐标分别为氧化还原电位(Eh)和电子活度的负对数(pe)，单位分别为 mV 和无量纲。图 1.2(a)、(b)分别为 As(III)和 As(V)在不同 pH 下的形态分布，横坐标为酸碱度(pH)，单位为无量纲；纵坐标为形态分布百分比，单位为%。由图 1.1 可知，水体中的 H<sub>3</sub>AsO<sub>3</sub> 分子可电离生成 H<sub>2</sub>AsO<sub>3</sub><sup>-</sup>(pK<sub>a1</sub>=9.2 时)、HAsO<sub>3</sub><sup>2-</sup>(pK<sub>a2</sub>=9.2 时)和 AsO<sub>3</sub><sup>3-</sup>(pK<sub>a3</sub>=12.7 时)，水体中的 H<sub>3</sub>AsO<sub>4</sub> 分子可电离生成 H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>(pK<sub>a1</sub>=2.3 时)、HAsO<sub>4</sub><sup>2-</sup>(pK<sub>a2</sub>=6.8 时)和 AsO<sub>4</sub><sup>3-</sup>(pK<sub>a3</sub>=11.6 时)。由图 1.2 可知，在天然水环境中 As(III)主要以分子态的 H<sub>3</sub>AsO<sub>3</sub> 形式存在，移动性高；As(V)主要以带负电荷的 H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>和 HAsO<sub>4</sub><sup>2-</sup>形式存在<sup>[10]</sup>。



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